

## PATENT ABSTRACTS OF JAPAN

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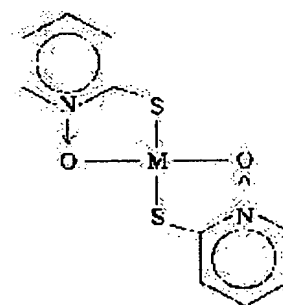
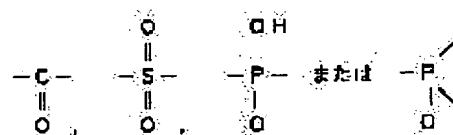
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## (54) ANTIFOULING COATING COMPOSITION

## (57)Abstract:

PROBLEM TO BE SOLVED: To obtain an antifouling coating compsn. which is excellent in persistently inhibiting the growth of marine organisms and has a good storage stability by compounding a hydrolyzable self-polishing resin having specific groups (e.g. carbonyl groups) at the side chains with cuprous oxide and a metal salt of bis(2-pyridinethiol-1-oxide).

SOLUTION: This compsn. contains at least one hydrolyzable self-polishing resin (A) which is prepd. by reacting a resin having groups of formula I at the side chains and an acid value of 30-350, an oxide, hydroxide, sulfide, or chloride of divalent copper or a copper ester of a monovalent org. acid, and a monovalent org. acid and has groups of the formula: -X-O-Cu-Y (wherein X is a group of formula I, pref. carbonyl; and Y is an org. acid residue) as the vehicle, cuprous oxide (B), and a metal salt of bis(2-pyridinethiol-1-oxide) (C) of formula II (wherein M is divalent Cu or Zn). The compounding ratios of ingredient B, ingredient C, and the sum of ingredients B and C are 5-60 wt.%, 0.1-30 wt.%, and 10-65 wt.%. respectively.



## LEGAL STATUS

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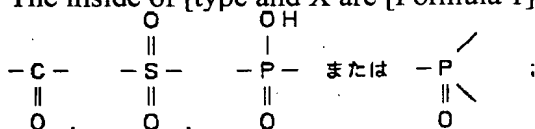
## CLAIMS

[Claim(s)]

[Claim 1] (i) It is a general formula (I) to a side chain.

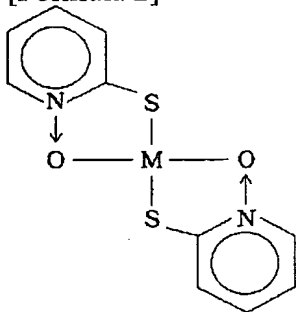
-X-O-Cu-Y (I)

The inside of [type and X are [Formula 1].



Y is at least one sort, the (ii) cuprous oxide, and (iii) formula (II) of the hydrolysis nature self-polish mold resin which has the radical expressed with] showing organic-acid residue.

[Formula 2]



It is an antifouling paint constituent containing the bis(2-pyridine thiol-1-oxide) metal salt expressed with [M expresses Cu or Zn of bivalence among a formula].

[Claim 2] The antifouling paint constituent according to claim 1 whose X is a carbonyl group.

[Claim 3] The antifouling paint constituent according to claim 1 or 2 whose resin which has the side chain of claims 1 or 2 is acrylic resin or polyester resin.

[Claim 4] An antifouling paint constituent given in either of claims 1, 2, or 3 whose sum total loadings of (ii) and (iii) the loadings in the coating of a cuprous oxide (ii) and a bis(2-pyridine thiol-1-oxide) metal salt (iii) are 5 - 60 % of the weight, and 0.1 - 30 % of the weight, respectively, and are 10 - 65 % of the weight among a coating.

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DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the marine paint constituent for sea aquatic life adhesion inhibition. It is related with the hydrolysis mold self-polish nature coating constituent which was excellent in especially hydrolysis nature, and was excellent in storage stability.

[0002]

[Description of the Prior Art] The coating of the hydrolysis nature self-polish mold which has the continuously excellent effectiveness as a coating constituent for preventing sea aquatic lives, such as acorn shells, a sea mussel, KOKEMUSHI, a sea squirt, and seaweed, adhering to rejection water spaces, such as a vessel and a sea structure, attracts attention recently. With the base resin which can hydrolyze this hydrolysis nature self-polish mold coating all over seawater, and can dissolve all over the sea, generally When base resin exfoliates in constant by the dissolution including the high compound of the inhibition effectiveness to the sea colonization adhesion object, while removing an affix, it is newly exposed continuously and the adhesion inhibitor distributed in base resin checks adhesion of a sea colonization adhesion object. The self-polish nature of a paint film can be controlled and adhesion inhibition ability can be made to maintain over a long period of time in this kind of constituent by designing the catabolic rate of hydrolysis nature resin, and the solubility of the water soluble resin generated by hydrolysis the optimal.

[0003] A thing typical as hydrolysis self-polish mold resin in the inside of such seawater is resin which contains the metal ester section of hydrolysis nature in a molecule. For example, the hydrolysis nature self-polish mold resin for antifouling paints which is shown to  $\text{-COO-M-OCOR}$  radical (M is the metal of bivalence and R is an alkyl group) and JP,8-209005,A by the  $\text{-COO-M-OH}$  radical, and is shown in JP,8-3484,A by  $\text{-COO-M-O-Si(R)}$  radical is proposed by JP,8-73536,A. When these resin is used as an antifouling paint constituent, generally the cuprous oxide is used as a sea aquatic life adhesion inhibitor. Although the paint film which hydrolyzes each of these coatings by being influenced of the ion of \*\*\*\*\* all over seawater, has self-polish nature, and has good sea aquatic life adhesion inhibition nature can be formed, even if storage stability is bad and very long, as for the coating which consists of these constituents, it has turned out hyperviscosity-ization or that it gels at extent which does not become useful within 2 or 3 hours when the worst within 2 or 3 days.

[0004] It has indicated using bis(2-pyridine thiol-1-oxide) copper salt as a sea aquatic life adhesion inhibitor in the hydrolysis mold self-polish mold coating constituent which combined with JP,8-269388,A the hydrolysis nature self-polish mold resin which has a moderate hydrolysis rate, and sea aquatic life adhesion inhibitor. However, about the stability of a coating, reference is not made at all by this invention.

[0005] The rosin which is the hydrophilic matter is blended with water-insoluble nature or the resin base of fine water solubility, gelation of a coating is prevented in the so-called autoclasis mold antifouling paint which makes sea aquatic life adhesion inhibition nature maintain by carrying out swelling collapse of the paint film, and in order to make adhesion inhibition ability maintain, the constituent which blended the 1st copper of oxidation with copper pilus thione is indicated. However, a hydrolysis nature self-polish mold coating is not described.

[0006] Moreover, it has proposed blending with JP,4-80269,A the ligand which can be configured to a metal as an approach of improving storage stability. Although surely storage stability is improved by this, by protecting a hydrolysis segment, the hydrolysis nature of resin original fell extremely this time, and the problem that long-term antifouling property ability is not obtained has arisen. Thus, the antifouling paint constituent with which resin and a cuprous oxide given in this invention were used together, and sea aquatic life adhesion inhibition nature was improved, and both the storage stability of resin and the hydrolysis nature of resin were improved is not obtained.

[0007]

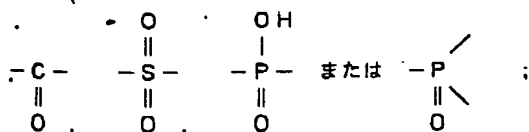
[Problem(s) to be Solved by the Invention] This invention is excelling in continuous sea aquatic life adhesion inhibition nature, and offering an antifouling paint constituent with good storage stability.

[0008]

[Means for Solving the Problem] This invention is a general formula (I) to the (i) side chain.

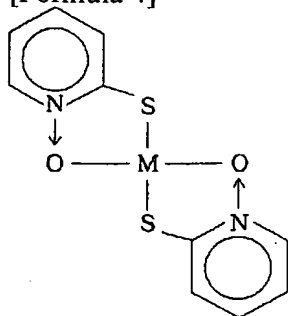
$\text{-X-O-Cu-Y (I)}$

The inside of [type and X are [Formula 3].



Y is at least one sort, the (ii) cuprous oxide, and (iii) formula (II) of the hydrolysis nature self-polish mold resin which has the radical expressed with] showing organic-acid residue.

[Formula 4]



It is related with the antifouling paint constituent containing the bis(2-pyridine thiol-1-oxide) metal salt expressed with [M expresses Cu or Zn of bivalence among a formula]. Especially this invention relates to the above-mentioned antifouling paint constituent whose X is a carbonyl group.

[0009] The above-mentioned constituent of this invention has the description of excelling in the storage stability of a coating by combination of a pilus thionic acid metal salt while discovering the adhesion inhibition nature which was excellent to adhesion of a sea aquatic life by containing the metal content resin and the cuprous oxide which became a hydrophilic property by hydrolysis all over seawater, and were equipped with self-polish nature.

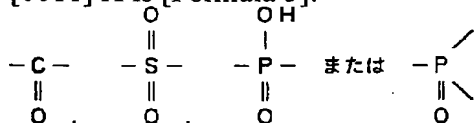
[0010]

[Embodiment of the Invention] The hydrolysis nature self-polish mold resin (i) used as a vehicle in the antifouling paint constituent of this invention is a general formula (I).

-X-O-Cu-Y (I)

It comes out and has the radical expressed as a side chain.

[0011] X is [Formula 5].



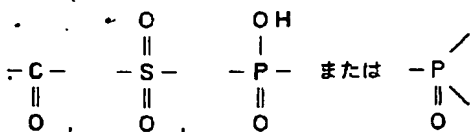
It comes out. Especially, especially a carbonyl group is desirable.

[0012] Y is organic-acid residue. The coating constituent of this invention may consist only of resin which has one kind of Y, and may also contain two or more kinds of resin with which Y differs. Organic-acid residue can illustrate mono-sulfonic acids, such as monocarboxylic acid; benzenesulfonic acid, such as an acetic acid, a propionic acid, butanoic acid, a lauric acid, stearin acid, linolic acid, oleic acid, a naphthenic acid, the chloroacetic acid, gifblaar poison, an abietic acid, phenoxyacetic acid, a valeric acid, dichlorophenoxyacetic acid, a benzoic acid, and a naphthoic acid, p-toluenesulfonic acid, dodecylbenzenesulfonic acid, a naphthalene sulfonic acid, and p-phenylbenzene sulfonic acid. It is the straight chain or branching alkyl carboxylic acid of a naphthenic acid and carbon numbers 4-20 preferably.

[0013] Moreover, as Y, although the above-mentioned organic-acid residue is desirable, a hydroxyl group or -O-Si (R) [R expresses a hydrogen atom, a halogen atom, a hydroxyl group, an organic radical, the ORGANO (Pori) siloxane radical, a silyl radical, sulfhydryl groups, or these substitution products]3 is effective in addition to it.

[0014] The trunk giant-molecule chain (base resin) which uses as a side chain the radical expressed with a general formula (I) is hydrophobicity comparatively, and in the condition of having this side chain, while it has the good paint film engine performance, after a side chain hydrolyzes, it becomes a hydrophilic property, and especially if it has the property which can be gradually dissolved from a paint film front face, it will not be restricted. As such resin, acrylic resin, polyester system resin, epoxy system resin, polyurethane resin, an acrylic modified epoxy resin, acrylic denaturation polyester resin, alkyd resin, and a fluororesin are mentioned. desirable -- acrylic resin and polyester resin -- it is acrylic resin especially preferably.

[0015] the hydrolysis nature self-polish nature resin of this invention -- the inside of the above-mentioned resin -- the acid number -- 30-350 -- it is preferably set to 60-300 -- as -- [Formula 6]



What was compounded so that the radical expressed with a formula (I) might be formed based on the resin which made the \*\* machine contain is suitable. That is, the hydrolysis nature resin of this invention is a general formula (III), when a trunk macromolecule is expressed with Rp.

Rp-X-O-Cu-Y (III)

It is come out and expressed.

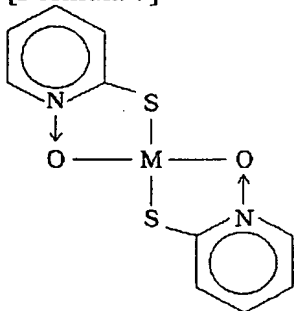
[0016] The example of the concrete manufacture approach of the hydrolysis self-polish nature resin of this invention is explained below. Which [ two ] the following approach may be used as a typical synthetic approach.

(i) Heating churning of the organic acid of the resin which contains a carboxyl group in the (a) side chain, the oxide of the copper of (b) bivalence, a hydroxide, a sulfide or a chloride, and (c) monovalence can be carried out below with the decomposition temperature of request copper ester content resin, decomposition purification of the by-product can be carried out by request, and the resin which has the copper ester section in a resin side chain can be obtained. As for the operating rate of the raw material in this reaction, it is desirable that (b) is 0.8-1.5Eq (especially preferably 1.0-1.2Eq), and (c) is 0.8-2Eq (especially preferably 1.0-1.5Eq) to 1Eq of acid radicals in resin (a). In addition, when choosing the monovalence organic acid of a low-boiling point and taking the reaction format accompanied by dehydration, since there is a danger of the organic acid of monovalence distilling out of a system with water, and a copper ester bond arising between resin, and producing a viscosity rise or gelation, it is desirable to use the amount of (c) more than the above.

[0017] Or the copper ester (e) of a monovalence organic acid and the organic acid (c) of monovalence are made for the (ii) side chain to react to the resin (a) which has a carboxyl group at the temperature below the decomposition temperature of a request product, and the copper ester section is introduced into a resin side-chain end by the ester exchange reaction. An acid comes out of for example, an acetic acid etc. out of a system with heating, and since there is a possibility of producing a metal ester bond between resin, it is necessary to make a reaction advance carefully at this reaction, when the boiling point of a univalent organic acid is low. Usually, 0.3-3Eq 0.4-2.5Eq and (c) of the amount of (e) are 1.0-1.5Eq preferably to 1Eq of acid radicals in resin (a). [ 0.8-2.0Eq ]

[0018] The bis(2-pyridine thiol-1-oxide) metal salt used by this invention is a formula (II).

[Formula 7]



It is the compound expressed with [M expresses Cu or Zn of bivalence among a formula].

[0019] The loadings in the coating of a cuprous oxide are 10 - 50 % of the weight preferably five to 60% of the weight. At less than 5 % of the weight, there is no antifouling effectiveness of a cuprous oxide, and if 60 % of the weight is exceeded, it will become the crack of a paint film, and the cause of generating of a crack. The loadings in the coating of a bis(2-pyridine thiol-1-oxide) metal salt (copper or zinc) are 0.5 - 20 % of the weight preferably 0.1 to 30% of the weight. At less than 0.1 % of the weight, the viscosity rise depressor effect under storage is not accepted, but if 30 % of the weight is exceeded, film reinforcement with the absorptivity of a paint film highly sufficient all over seawater is unmaintainable. The sum total loadings of a cuprous oxide and a bis(2-pyridine thiol-1-oxide) metal salt are 10 - 65 % of the weight among a coating, and are 11 - 55 % of the weight preferably.

[0020] In addition to the above-mentioned indispensable component, a stain proofing agent can be further blended with the antifouling paint constituent of this invention if needed. An organic compound can be illustrated although the inorganic compound which are shown by making it below as a stain proofing agent which can be used, a metal content organic compound, and a metal are not included. As an inorganic system compound, copper compounds, such as copper powder, thiocyanic acid copper, copper carbonate, a copper chloride, and a copper sulfate, a zinc sulfate, a zinc oxide, a nickel sulfate, copper nickel alloys, etc. are mentioned, for example.

[0021] As an organic compound containing a metal, there are an organic copper system compound, an organic nickel system compound, an organic zinc system compound, etc., in addition MANNEBU, MANSEBU, propineb, etc. can be used, for example. As an organic copper system compound, dimethyl dithiocarbamic acid nickel etc. is mentioned as

an organic nickel system compound, and oxine copper, copper nonylphenolsulfonate, a kappa bis(ethylenediamine)-screw (dodecylbenzene sulfonate), bis(pentachlorophenol acid) copper, etc. are mentioned for carbamic acid zinc, zinc dimethyldithiocarbamate, ethylene screw dithiocarbamic acid zinc, etc. as an organic zinc system compound, respectively.

[0022] As an organic compound which does not contain a metal, there is a thing of N-trihalomethyl thio phthalimide, dithiocarbamic acid, N-aryl maleimide, the 3-permutation-amino -1, 3-thiazolidine -2, 4-dione, dithiocyano compound, triazine compound, and others, for example. As an N-trihalomethyl thio phthalimide, N-TORIKUORO methylthio phthalimide, N-fluoro dichloro methylthio phthalimide, etc. are mentioned, and bis (dimethylthiocarbamoyl) disulfide, N-methyl ammonium dithiocarbamate, ethylene bis(dithiocarbamic acid) ammonium, thione, etc. are mentioned as dithiocarbamic acid, respectively.

[0023] As N-aryl maleimide, N-(2, 4, 6-TORIKUORO phenyl) maleimide, N-4-tolyl maleimide, N-3-chlorophenyl maleimide, N-(4-n-butylphenyl) maleimide, N-(ANIRINO phenyl) maleimide, N-(2, 3-xylyl) maleimide, etc. are mentioned.

[0024] As 3-permutation amino -1, 3-thiazolidine -2, and 4-dione 3-benzylidene amino -1, 3-thiazolidine -2, 4-dione, 3-(4-methyl benzilideneamino)-1, 3-thiazolidine -2, 4-dione, 3-(2-hydroxy benzilideneamino)-1, 3-thiazolidine -2, 4-dione, 3-(4-dimethylamino benzylidene amino)-1, 3-thiazolidine -2, 4-dione, 3-(2, 4-dichloro benzyl DIN amino)-1, 3-thiazolidine -2, 4-dione, etc. are mentioned.

[0025] As dithiocyano compound, a dithio cyano methane, dithio cyano ethane, 2, and 5-dithio cyano thiophene etc. is mentioned, and 2-methylthio-4-t-butylamino-6-cyclobutylpropylamino-s-triazine etc. is mentioned as triazine compound, respectively.

[0026] As an organic compound which does not contain other metals 2, 4, 5, 6-tetra-chloro isophthalonitrile, N, and N-dimethyl dichlorophenyl urea, 4 Five - Dichloro-2-N-octyl-3-(2H) iso thiazolone, N and N-dimethyl-N'-phenyl-(N-fluoro dichloro methylthio) sulfamide, Tetramethylthiuramdisulfide, a 3-iodine-2-propynyl butyl carbamate, 2-(methoxycarbonylamino) benzimidazole 2, 4, and 5, a 6-tetra-chloro-4-(methyl sulfonyl) pyridine, a diiodomethyl PARATORIRU sulfone, 2-(4-thiazolyl) benzimidazole triphenyl boron pyridine, etc. are mentioned. It is also possible in these to use together one sort or two sorts or more if needed.

[0027] Other additives used for the following solvents, a hydrolysis regulator, a plasticizer, a pigment, and a dripping inhibitor and other antifouling paints may be further blended with the antifouling paint constituent of this invention if needed. As a solvent, a xylene, toluene, benzene, ethylbenzene, a cyclopentane, Hydrocarbons, such as an octane, a heptane, a cyclohexane, and white spirit; Dioxane, A tetrahydrofuran, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, Ethylene glycol wood ether, ethylene glycol monobutyl ether, Ethylene glycol dibutyl ether, the diethylene-glycol monomethyl ether, Ether, such as diethylene glycol monoethyl ether; Butyl acetate, Propyl acetate, benzyl acetate, ethylene glycol monomethyl ether acetate, Ester, such as ethylene glycol monoethyl ether acetate; there are alcohols, such as ketones; n-butanols, such as methyl isoamyl ketone and methyl isobutyl ketone, and propyl alcohol, etc.

[0028] As a hydrolysis regulator, there are chlorinated paraffin, polyvinyl ether, a polypropylene separation, partial hydrogenation terphenyl, polyvinyl acetate, Pori (meta) acrylic-acid alkyl ester, polyether polyol, polyester polyol, an alkyd resin, polyester resin, a polyvinyl chloride, etc.

[0029] As a plasticizer, phthalate ester plasticizer; diisobutyl adipates, such as dioctyl phthalate, dimethyl phthalate, and dicyclohexyl phthalate, Aliphatic series dibasic-acid-ester system plasticizers, such as a dibutyl sebacate; Diethylene glycol dibenzoate, Glycol ester system plasticizers, such as pentaerythritol alkyl ester; A TORIKUREJIRURIN acid, Phosphoric ester system plasticizers, such as a trichloroethyl phosphoric acid; Epoxidized soybean oil, epoxy system plasticizers [, such as epoxy stearin acid octyl, ]; -- organic tin system plasticizers [, such as a dioctyl tin RAURI rate and a dibutyl tin RAURI rate, ]; -- in addition to this, there are trimellitic acid trioctyl, camphor, thoria cetylene, etc.

[0030] As a pigment, there are color pigments, such as extender; titanium oxide, such as baryte, precipitated barium sulphate, talc, clay, chalk, a silica white, an alumina white, a titanium white, and a bentonite, oxidation zircon, a basic lead sulfate, tin oxide, carbon black, a graphite, red ocher, chrome green, emerald green, and a copper phthalocyanine blue.

[0031] As other additives, there are organic monobasic acids, such as rosin, phthalic-acid monobutyl, and succinic-acid mono-octyl, camphor, castor oil, etc. The constituent of this invention can be adjusted by the well-known approach in itself in the coating manufacturing-technology field. On the occasion of preparation, a well-known machine, for example, a ball mill, HEBURUMIRU, a roll mill, a speed run mill, etc. can be used.

[0032] Especially the approach of forming a paint film using the coating constituent of this invention is not restricted, and the same approach as the conventional antifouling paint can be used for it. for example, the coating constituent of this invention -- an underwater structure (for example, a vessel and harbor facilities --) On base material front faces, such as a buoy, a pipeline, a bridge, a submarine base, a culture network, and a fixed net, direct, To a base material, or primers; oiliness rust-proofings, such as a wash primer and a zinc epoxy system shop primer, Under coat primers, such as a chlorinated-rubber system and an epoxy system; A long-oil-length phthalic resin system, Middle coats, such as a chlorinated-rubber system and an epoxy system, the monolayer paint film which applied top coat, respectively and

was formed, It can apply to the base material front face in which the double layer paint film which applied the coating of a primer and an under coat primer, and was formed and the primer, the under coat primer, and the double layer paint film formed by carrying out the sequential paint of the Nakagami coating coating were prepared with means, such as brush coating, blasting coating, roller coating, and immersion. Generally 40-500 micrometers of the spreading thickness can be preferably made into within the limits of 60-300 micrometers as a dry paint film. Desiccation of a paint film can be performed at a room temperature.

[0033] It is considered to be based on the following mechanisms of action that the antifouling paint constituent of this invention is excellent in storage stability. Although apparent giant-molecule-ization takes place and it becomes the cause of thickening and hydrolysis inhibition by what the copper ion of metal \*\*\*\* in resin has a cuprous oxide and an intermolecular interaction for (false bridge formation is carried out), when the metal ion in a pilus thione metal salt carries out inhibition control of the formation of false bridge formation, it is thought by making a pilus thione metal salt live together that the stable storage stability and the stable hydrolysis function of resin original are made securable.

[0034]

[Example] The following examples explain this invention to a detail concretely further.

The xylene 64 weight section and the n-butanol 16 weight section are added to 4 opening flask equipped with the manufacture agitator of resin varnish A, a cooler, a temperature controller, nitrogen installation tubing, and a dropping funnel, and it keeps at 100 degrees C. Uniform dropping of the mixed liquor of the ethyl-acrylate 58.3 weight section, the cyclohexyl methacrylate 15 weight section, the NK-ester M-90G (new Nakamura chemistry company make: methacrylic-acid methoxy polyethylene-glycol ester) 10 weight section, the acrylic-acid 16.7 weight section, and the t-butylperoxy-2-ethylhexanoate 2 weight section was carried out over 3 hours into this solution. It was kept warm for 30 minutes after dropping termination. Then, uniform dropping of the mixed liquor of the xylene 16 weight section, the n-butanol 4 weight section, and the t-butylperoxy-2-ethylhexanoate 0.2 weight section was carried out over 30 minutes, and it was kept warm after dropping termination for 30 minutes per hour. The varnish A of the solid content of 49.8 % of the weight in the obtained resin solution, the viscosity of 4.4poise, and the resin (solid content; similarly solid content is expressed below) acid number 130 was obtained.

[0035] Into the same reaction container as the example of example varnish of manufacture A manufacture of resin varnish B, the xylene 64 weight section and the n-butanol 16 weight section are added, and it keeps at 100 degrees C. Uniform dropping of the mixed liquor of the 2-ethylhexyl methacrylate 45.8 weight section, the cyclohexyl methacrylate 15 weight section, the NK-ester M-90G (new Nakamura chemistry company make; methacrylic-acid methoxy polyethylene-glycol ester) 20 weight section, the acrylic-acid 19.2 weight section, and the t-butylperoxy-2-ethylhexanoate 2.0 weight section was carried out over 3 hours into this solution, and it was kept warm after dropping termination for 30 minutes per hour. The solid content in the obtained resin solution obtained the varnish B of the viscosity of 19.5poise, and the resin (solid content) acid number 150 50.5% of the weight.

[0036] The preparation agitator of hydrolysis nature self-polish mold resin [a], nitrogen installation tubing, a reflux condenser, In 4 opening flask equipped with the decanter and the temperature controller, the varnish A100 weight section, The copper acetate 23.1 weight section, the "EKUASHIDDO SA-13" (Idemitsu petroleum company make; 6,6-dimethyl-2-methyl-2-isobutyl-heptane carboxylic acid) 24.4 weight section, The xylene 140 weight section was added, it heated at 130 degrees C, and the acetic acid generated as a reaction advances was removed with the solvent. The terminal point of a reaction carried out the quantum of the acetic acid in an outflow solvent, and determined it. The solid content of the obtained metal content resin varnish was 40.2 % of the weight, and viscosity was 7.5poise.

[0037] Into the same reaction container, the varnish A100 weight section, the copper acetate 24.0 weight section, the naphthenic-acid 32.4 weight section, and the xylene 100 weight section were added with having used it for preparation of the preparation above-mentioned resin [a] of hydrolysis nature self-polish mold resin [b], it heated at 130 degrees C, and the acetic acid was removed with the solvent. Solid content was 32.5 % of the weight, and the viscosity of the obtained metal content resin varnish was 12.9poise.

[0038] Into the same reaction container, the varnish B100 weight section, the copper acetate 28 weight section, the naphthenic-acid 37.5 weight section, and the xylene 50 weight section were added with having used it for preparation of the preparation above-mentioned resin [a] of hydrolysis nature self-polish mold resin [c], it heated at 130-140 degrees C, and the acetic acid was removed with the solvent. The solid content of the obtained metal content resin varnish was 17.6poise in viscosity 35.3% of the weight.

[0039] Example As a cuprous oxide and a bis(2-pyridine thiol-1-oxide) metal (zinc or copper) salt were blended with hydrolysis nature self-polish mold resin [a]- [c] prepared by the one to 12 above and having been further described in Table 1, a plasticizer, other stain proofing agents, the pigment, the dripping inhibitor, and the solvent were blended, and the antifouling paint constituent of examples 1-12 was prepared. The storage stability and antifouling property of a coating which were acquired were examined, and the result was shown in Table 1.

[0040]

[Table 1]



(重量部)

実施例	1	2	3	4	5	6	7	8	9	10	11	12
加水分解性 自己研磨型樹脂	(a)	(a)	(a)	(b)	(a)	(a)	(c)	(a)	(b)	(b)	(a)	(c)
樹脂量	40	40	40	49.5	40	40	45.6	40	49.5	49.5	40	45.6
可塑剤(塩素化パラフィン)	4	4	4	4	4	4	4	4	4	4	4	4
防汚 剤	亜酸化銅	40	40	40	40	40	40	40	40	40	40	40
	ZnPT <sup>1)</sup>	5		5	5	5	5					
	CuPT <sup>1)</sup>		5					5	5	5	5	5
	2,4,5,6-ジチオクロム イソチオニル			5			3	5			3	
	N,N-ジチオクロム フェニル尿素				5	3			5		3	
	ジシロキシジメチルポリメチル シロキサン					5				5		
	顔料						5					5
溶剤	ベンガラ	5	5	5	5	5	5	5	5	5	5	5
	タルク						5					5
溶剤	メチルイソブチルケトン	2	2	2	2	2	2	2	2	2	2	2
	キシレン	4	4	4		4	4	4			4	
タレ防止剤 <sup>2)</sup>		2	2	2	2	2	2	2	2	2	2	2
塗料 特性	貯蔵安定性											
	20℃ 3カ月後	良好	良好	良好	良好	良好	良好	良好	良好	良好	良好	良好
	40℃ 3カ月後	良好	良好	良好	良好	良好	良好	良好	良好	良好	良好	良好
	塗膜の長期防汚性能											
	浸漬月数 3	0	0	0	0	0	0	0	0	0	0	0
	6	0	0	0	0	0	0	0	0	0	0	0
	9	0	0	0	0	0	0	0	0	0	0	0
	12	0	0	0	0	0	0	0	0	0	0	0
	18	0	0	0	0	0	0	0	0	0	0	0
	24	0	0	0	0	0	0	0	0	0	0	0
	30	0	0	0	0	0	0	0	0	0	0	0
	36	0	0	0	0	0	0	0	0	0	0	0

1) ZnPT: エス(2-ピリジンチオール-1-オキシド)Zn、CuPT: エス(2-ピリジンチオール-1-オキシド)Cu

2) 商品名「ディスパロン A630-20X」(楠本化成(株)製)

[0041] Example of a comparison To the hydrolysis nature self-polish mold resin [a] prepared by the one to 7 above, as shown in Table 2, the cuprous oxide or the bis(2-pyridine thiol-1-oxide) metal (zinc or copper) salt was blended, and the antifouling property coating constituent was prepared. The storage stability of a coating constituent was also indicated to Table 2.

[0042]

[Table 2]

(重量部)

比較例		1	2	3	4	5	6	7
加水分解性 自己研磨型樹脂		(a)	(a)	(a)	(a)	(a)	(a)	(a)
樹脂量		40	40	40	40	40	40	40
可塑剤(塩素化パラフィン)		4	4	4	4	4	4	4
防汚剤	亜酸化銅	30	40	50				40
	ZnPT				5	5		
	CuPT						5	
	2,4,5,6-テトラクロロ イソフタロニトリル				5		5	
	N,N-ジメチル-2,6-ピリ ジニウム				5		5	
	フェニル尿素				5		5	
	ジメチルジメチルジメチル ジメチルジメチルジメチル				5		5	
顔料	亜鉛華							
	ベンガラ	5	5	5	5	5	5	5
溶剤	タルク							
	メチルイソブチルケトン	2	2	2	2	2	2	2
タレ防止剤	キシレン	4	4	4	4	4	4	4
	タレ防止剤	2	2	2	2	2	2	2
塗料特性	貯蔵安定性							
	20℃ 3カ月後	ゲル	ゲル	ゲル	良好	良好	良好	
	40℃ 3カ月後	ゲル	ゲル	ゲル	良好	良好	良好	
	塗膜の長期防汚性能							※
	浸漬月数 3	0	0	0	0	0	0	0
	6	0	0	0	0	0	0	0
	9	10	10	10	0	0	0	0
	12	10	10	10	0	0	0	0
	18	20	20	10	0	5	0	0
	24	30	20	10	5	5	5	0

※：比較例7の塗膜の防汚性能試験用塗板は製造直後の塗料を塗布して作成した。

[0043] In the trial of the appraisal method above of a coating property, it estimated "Look like [ a following approach and a following valuation basis ] the storage stability of a coating, and the long-term antifouling property ability of a paint film."

[Storage stability]

1) Appraisal method: The viscosity immediately after coating manufacture was measured using the Stormer viscosimeter (coating temperature of 25 degrees C). Next, this coating was stored at the temperature of 20 degrees C and 40 degrees C, respectively, and change of viscosity (25 degrees C) was measured with time.

2) Criterion: The viscosity change three months after storage made good the thing within 20Ku(s) (measurement temperature: 25 degrees C).

[Long-term antifouling property ability of a paint film]

1) Appraisal method: The paint film was formed using the coating for room temperature (20 degrees C) storage one month. To the color card which has applied the anticorrosion paint to the sandblasting processing steel plate beforehand, each coating was applied so that desiccation thickness might be set to 200 micrometers, and it was dried, and the paint film for evaluation was obtained to it. This sample was hung to the raft for a test of the Hyogo Aioi inside of the bay, it was immersed all over the sea, and antifouling property ability was examined.

2) Criterion: After fixed period immersion, it pulled up and the area from which the color card is soiled with viewing by foulings was expressed with %.

[0044]

[Effect of the Invention] A 1 liquid type hydrolysis mold self-polish nature ship bottom paint with good storage stability can be obtained without according to this invention, being able to control sharply thickening under storage of the antifouling paint which combined metal content hydrolysis mold resin and a cuprous oxide, consequently spoiling the hydrolysis nature of resin original.

[Translation done.]